

Solid-Source Doping of Float-Zoned Silicon with B, N, O, and C

Preprint

T.F. Ciszek

*To be presented at the 13th Workshop on Crystalline
Silicon Solar Cell Materials and Processes
Vail, Colorado
August 10-13, 2003*



NREL

National Renewable Energy Laboratory

1617 Cole Boulevard
Golden, Colorado 80401-3393

NREL is a U.S. Department of Energy Laboratory
Operated by Midwest Research Institute • Battelle • Bechtel

Contract No. DE-AC36-99-GO10337

NOTICE

The submitted manuscript has been offered by an employee of the Midwest Research Institute (MRI), a contractor of the US Government under Contract No. DE-AC36-99GO10337. Accordingly, the US Government and MRI retain a nonexclusive royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for US Government purposes.

This report was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or any agency thereof.

Available electronically at <http://www.osti.gov/bridge>

Available for a processing fee to U.S. Department of Energy
and its contractors, in paper, from:

U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831-0062
phone: 865.576.8401
fax: 865.576.5728
email: reports@adonis.osti.gov

Available for sale to the public, in paper, from:

U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
phone: 800.553.6847
fax: 703.605.6900
email: orders@ntis.fedworld.gov
online ordering: <http://www.ntis.gov/ordering.htm>



Printed on paper containing at least 50% wastepaper, including 20% postconsumer waste

Solid-Source Doping of Float-Zoned Silicon with B, N, O, and C

T. F. Ciszek*

National Renewable Energy Laboratory, Golden, CO 80401 USA

(*address after 9/1/03: www.siliconsultant.com, P.O. Box 1453, Evergreen, CO 80437 USA)

Abstract

We report on a solid-source method to introduce dopants or controlled impurities directly into the melt zone during float-zone growth of single- or multicrystalline ingots. Unlike the Czochralski (CZ) growth situation, float zoning allows control over the levels of some impurities (O, C) that cannot be avoided in CZ growth or ingot casting. But aside from impurity studies, the method turns out to be very practical for routine p-type doping in semicontinuous growth processes such as float-zoning, electromagnetic casting, or melt-replenished ribbon growth. Equations governing dopant incorporation, dopant withdrawal, and N co-doping are presented and experimentally verified. Doping uniformity, and doping initiation and withdrawal time constants are also reported. The method uses nontoxic source materials and is flexible with quick turnaround times for changing doping levels. Boron p-type doping with nitrogen co-doping is particularly attractive for silicon lattice strengthening against process-induced dislocation motion and also allows greater freedom from incorporation of Si self-interstitial cluster or A and B swirl-type defects and “D”-type microdefects than nitrogen-free p-type material.

Introduction

Float-zoned (FZ) silicon crystals (or other continuous, melt-replenished Si materials such as electromagnetically cast ingots, melt-replenished ribbons, or rapidly solidified continuous ribbons on a substrate) are doped by different methods depending on the dopant's segregation coefficient. If $k \ll 1$ (e.g., Ga dopant or N impurity in Si), it is best to place all dopant at the starting end of the feed rod or growth process. If $k \approx 1$ (e.g., B dopant or O impurity in Si), it is best to add the impurity uniformly and continuously as growth progresses. The choices for continuous dopant addition have traditionally been to either predope the feedstock uniformly (this sometimes involves long scheduling times and is somewhat inflexible) or to dope from the gas phase (e.g., with diborane during growth). Diborane is exceptionally toxic and requires stringent safety measures. Figure 1 summarizes doping strategies and introduces our solid-source method. Its applicability to high k (~ 1 , e.g., B, O), low k ($\sim 10^{-4}$, e.g., N), and intermediate k ($\sim 10^{-2}$, e.g., C) materials is discussed and characterized in the subsequent sections.

Experimental Procedure

For single crystals, a $\langle 100 \rangle$ seed orientation was used and the initial growth was necked to produce dislocation-free crystals. The feedstock was undoped polycrystalline silicon rods with resistivity $> 5,000 \Omega\text{-cm}$. The growth experiments were carried out in argon. The zone melting was done with an induction coil operating at 2 MHz. A usual growth rate was $0.33 \text{ cm} \cdot \text{min}^{-1}$, with a rotation rate of 10-15 rpm.

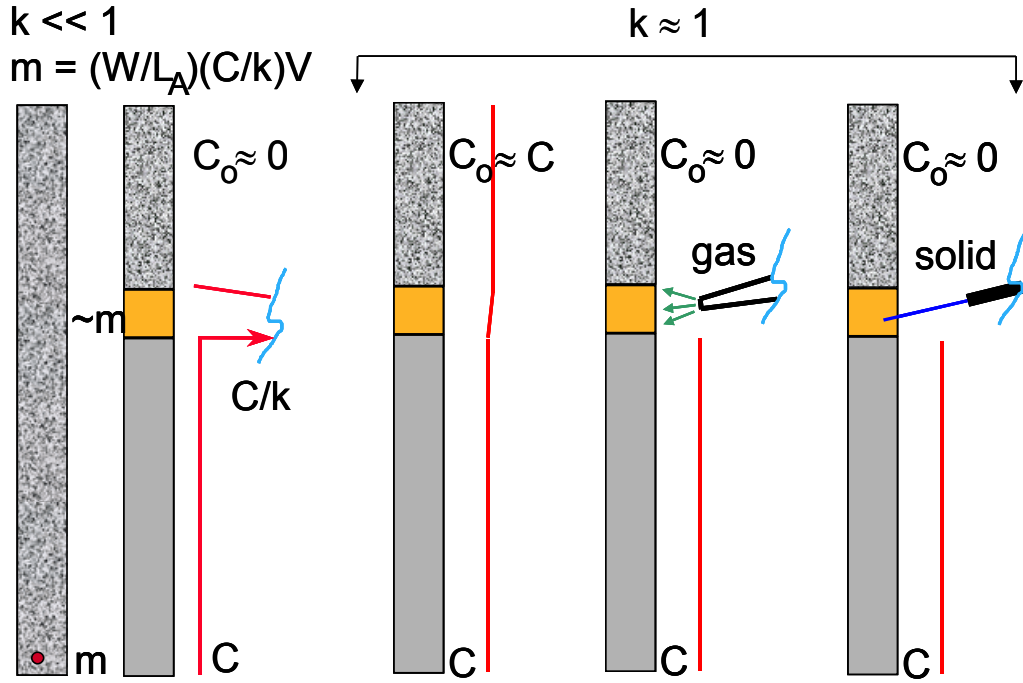


Fig. 1. Schematic representation of FZ doping strategies for $k \ll 1$ (pill doping with mass m at origin: W = atomic weight, L_A = Avogadro's No., C = desired concentration, k = effective segregation coefficient, V = melt volume); and for $k \approx 1$ (predoped feed, gas doping, and the solid-source method discussed in more detail in this manuscript).

Thin, long slivers of high-purity pyrolytic boron nitride were cut, cleaned in a mixed acid etch ($3\text{CH}_3\text{COOH} : 1\text{HF} : 2\text{HNO}_3$), and mounted on a translatable rod, which allowed the sliver tip to be inserted into the molten zone. This was the solid source for boron and nitrogen doping. High-purity fused quartz rods were used for O doping, and vitreous carbon slivers were used for C doping. The immersion was done manually with the sliver or rod attached to a metal rod passing through an "O"-ring-sealed connector in the chamber wall. The source was inserted radially, beneath the RF coil. Figure 2 is a photograph showing the doping arrangement for the particular case of O, N, and B co-doping a $\langle 100 \rangle$ dislocation-free FZ silicon crystal. Here, a $0.8 \text{ } \Omega\text{-cm}$ B-doped crystal containing $N_B \approx 2 \times 10^{16} \text{ atoms}\cdot\text{cm}^{-3}$ and $N_O \approx 8 \times 10^{16} \text{ atoms}\cdot\text{cm}^{-3}$ was produced with a

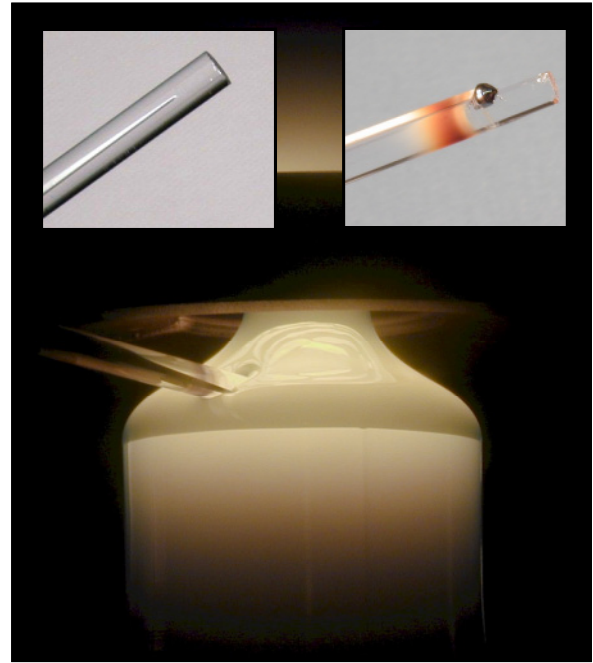


Fig. 2. B, N, and O co-doping a FZ crystal. The insets show the BN and SiO_2 solid sources before growth (left) and after growth (right).

gradually changing mid- 10^{15} atoms·cm⁻³ level for N_N (N is concentration and the subscript refers to the species). A 0.3-cm-diameter high-purity fused quartz rod was immersed 0.6 cm into the melt zone in conjunction with a thin BN sliver immersed 0.2 cm.

Our dopant incorporation model equation is

$$C_o = 4AD/\pi d^2 v, \quad (1)$$

where C_o is the uniform dopant concentration entering the melt zone (atoms·cm⁻³), A is the surface area (cm²) of the immersed solid source, D is the dissolution rate (atoms·cm⁻²·min⁻¹) of the source's doping component in molten silicon, d is the crystal diameter (cm), and v is the crystal growth rate (cm·min⁻¹). A one-time determination of D with the other parameters known allows eq. (1) to be used to calculate the A required for a desired N .

Results

Table I gives the D values that we have determined for the solid sources mentioned earlier, in units atoms·cm⁻²·min⁻¹. They depend on specific experimental conditions and are subject to error from imprecise knowledge of A . The estimated accuracy of the D values is about 10% for 3.4-cm-diameter float-zoned crystal growth. It is best to determine the values within the set of experimental conditions that will be used in a particular growth configuration.

Table I. D Values for B, N, O, and C

Dopant	B	N	O	C
D	3.7×10^{19}	3.7×10^{19}	2.3×10^{17}	9.7×10^{18}

Some of the main features of solid-source B doping from a pyrolytic BN source can be deduced from Fig. 3. A 3.4-cm-diameter, dislocation-free, <100> FZ crystal was grown at 0.32 cm·min⁻¹ from a 3.4-cm-diameter feed rod that had a resistivity of 5,000 Ω·cm or greater. After 7.5 cm of undoped growth, a 0.01-cm x 0.015-cm cross-section pyrolytic BN sliver was inserted about 0.15 cm into the melt zone. After 4.3 cm of additional growth, the immersion depth was increased to about 0.4 cm for another 4 cm of growth. Then the doping sliver was withdrawn. The resultant longitudinal resistivity profile of the crystal (as measured by a linear 4-point probe on a flat surface ground along the length of the crystal) is shown. The time constant for reaching uniform (0.22 Ω·cm or 9×10^{16} atoms·cm⁻³) B doping, starting from undoped growth, is about 3.2 min. The time constant for changing from one uniform B doping level (0.22 Ω·cm) to another (0.12 Ω·cm or 2.1×10^{17} atoms·cm⁻³) is about 2.4 min. The resistivity uniformity is about ± 9% in each segment. The profile after withdrawal of the BN (at 16.9 cm) fits an equation of the type

$$\rho = \rho_o e^{(k_B/L)z}, \quad (2)$$

as expected, with a fit standard error of 0.05 (and a coefficient of determination, r^2 , of 0.9995) for $k_B/L = 0.795$. Here ρ is resistivity, ρ_o is the resistivity at the point of dopant withdrawal, L is the effective zone length (cm), and z is the position after withdrawal (cm). The fitted value of k_B/L is consistent with $k_B = 0.9$ and $L = 1.13$ cm. L is the length the zone would be if all of the melt was in a right circular cylinder of diameter d . Radial resistivity profiles for a 5.2-cm-diameter, dislocation-free, <100> crystal doped to 1.3 Ω·cm are shown in Fig. 3 for positions 2 and 8 cm after dopant insertion. At 8 cm, the doping uniformity is ±0.03 Ω·cm or 2%.

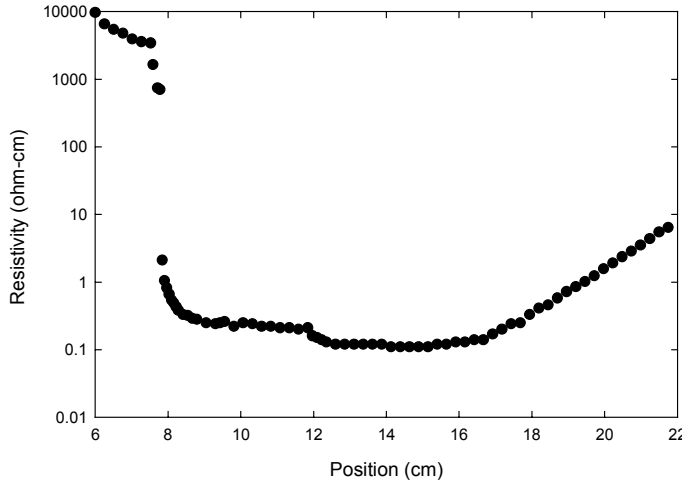


Fig. 3. Doping profile for insertion, change of immersed depth, and withdrawal of BN source.

Pfann's zoning equation:

$$N_N(z) = C_o[1-(1-k_N)e^{-k_N z/L}] = N_B[1-(1-k_N)e^{-k_N z/L}] = (4AD/\pi d^2 v)[1-(1-k_N)e^{-k_N z/L}]. \quad (3)$$

One-meter-long crystals can be grown with $\rho \geq 0.3 \Omega\text{-cm}$ without exceeding the N solubility limit of $4.5 \times 10^{15} \text{ atoms} \cdot \text{cm}^{-3}$. N is essentially electrically inactive as an n-type dopant. Nitrogen below the solubility limit is beneficial. It provides mechanical strengthening analogous to the way O does for CZ crystals, but at 100x lower concentration levels. It also allows swirl-defect-free growth at a larger range of growth rates than is the case for N-free crystals.

C doping is also governed by an equation analogous to eq. (3). Figure 5 shows that a nearly linear $N_C(z)$ distribution can be obtained by solid-source doping with a vitreous C sliver.

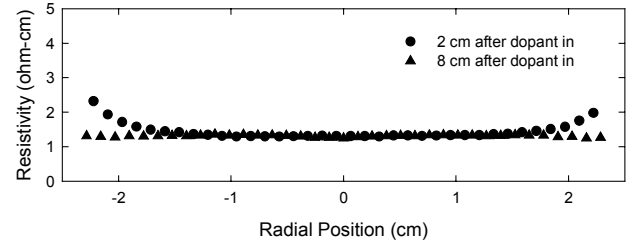


Fig. 4. Radial resistivity profiles for two locations along a 5.2-cm-dia. BN-doped crystal.

Of course, both nitrogen and boron enter the growing crystal during solid-source BN doping. Although k_B is about 0.9, a much lower value of $k_N = 7 \times 10^{-4}$ is characteristic of N in liquid silicon. The distribution of nitrogen along a BN-doped crystal, $N_N(z)$, can be obtained from

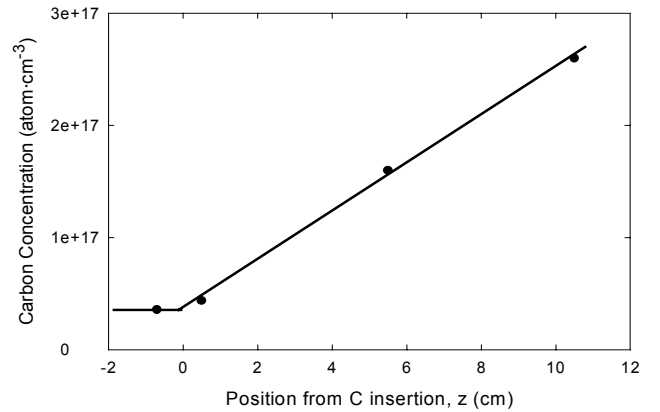


Fig. 5. Solid-source C doping

Summary and Discussion

A solid-source doping method for boron doping from a pyrolytic BN source has been described. It is applicable for B doping concentrations $\leq 6 \times 10^{16} \text{ atoms} \cdot \text{cm}^{-3}$, corresponding to $\rho \geq 0.3 \Omega\text{-cm}$ in meter-long crystals. Nitrogen incorporation below the solubility limit is desirable in FZ crystals for mechanical strengthening and point-defect control. This doping method has the benefit of nitrogen incorporation and allows B doping from a nontoxic source compared to diborane gas that is usually used for doping. Solid-source O and C doping were also described. Co-doping with B, N, and O was demonstrated. Equations for dopant intake into the melt, dopant withdrawal, and dopant distribution along the crystal were developed and experimentally verified.

REPORT DOCUMENTATION PAGE			<i>Form Approved</i> OMB NO. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE August 2003	3. REPORT TYPE AND DATES COVERED Conference Paper		
4. TITLE AND SUBTITLE Solid-Source Doping of Float-Zoned Silicon with B, N, O, and C: Preprint			5. FUNDING NUMBERS PVP34801	
6. AUTHOR(S) T.F. Ciszek				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) National Renewable Energy Laboratory 1617 Cole Blvd. Golden, CO 80401-3393			8. PERFORMING ORGANIZATION REPORT NUMBER NREL/CP-520-34604	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION/AVAILABILITY STATEMENT National Technical Information Service U.S. Department of Commerce 5285 Port Royal Road Springfield, VA 22161			12b. DISTRIBUTION CODE	
13. ABSTRACT (<i>Maximum 200 words</i>): We report on a solid-source method to introduce dopants or controlled impurities directly into the melt zone during float-zone growth of single- or multicrystalline ingots. Unlike the Czochralski (CZ) growth situation, float-zoning allows control over the levels of some impurities (O, C) that cannot be avoided in CZ growth or ingot casting. But aside from impurity studies, the method turns out to be very practical for routine p-type doping in semicontinuous growth processes such as float-zoning, electromagnetic casting, or melt-replenished ribbon growth. Equations governing dopant incorporation, dopant withdrawal, and N co-doping are presented and experimentally verified. Doping uniformity and doping initiation and withdrawal time constants are also reported. The method uses nontoxic source materials and is flexible with quick turnaround times for changing doping levels. Boron p-type doping with nitrogen co-doping is particularly attractive for silicon lattice strengthening against process-induced dislocation motion and also allows greater freedom from incorporation of Si self-interstitial cluster or A and B swirl-type defects and "D"-type microdefects than nitrogen-free p-type material.				
14. SUBJECT TERMS: photovoltaics; solid-source method; Czochralski (CZ) silicon; float-zone; electromagnetic casting; melt-replenished ribbon growth			15. NUMBER OF PAGES	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL	